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THE SILICON ISOTOPE COMPOSITION OF THE UPPER CONTINENTAL CRUST

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ABSTRACT

The upper continental crust (UCC) is the major source of silicon (Si) to the oceans and yet its isotopic composition is not well constrained. In an effort to investigate the degree of heterogeneity and provide a robust estimate for the average Si isotopic composition of the UCC, a representative selection of well-characterised, continentally-derived clastic sediments have been analysed using high-precision MC-ICPMS.

Analyses of loess samples define a narrow range of Si isotopic compositions ($\delta^{30}\text{Si} = -0.28$ to -0.15 ‰). This is thought to reflect the primary igneous mineralogy and predominance of mechanical weathering in the formation of such samples. The average loess $\delta^{30}\text{Si}$ is -0.22 ± 0.07 ‰ (2 s.d.), identical to average granite and felsic igneous compositions. Therefore, minor chemical weathering does not resolvably affect bulk rock $\delta^{30}\text{Si}$, and loess is a good proxy for the Si isotopic composition of unweathered, crystalline, continental crust.

The Si isotopic compositions of shales display much more variability ($\delta^{30}\text{Si} = -0.82$ to 0.00 ‰). Shale Si isotope compositions do not correlate well with canonical proxies for chemical weathering, such as CIA values, but do correlate negatively with insoluble element concentrations and Al/Si ratios. This implies that more intensive or prolonged chemical weathering of a sedimentary source, with attendant desilicification, is required before resolvable negative Si isotopic fractionation occurs. Shale $\delta^{30}\text{Si}$ values that are more positive than those of felsic igneous rocks most likely indicate the presence of marine-derived silica in such samples.

Using the data gathered in this study, combined with already published granite Si isotope analyses, a weighted average composition of $\delta^{30}\text{Si} = -0.25 \pm 0.16$ ‰ (2 s.d.) for the UCC has been calculated.

Keywords: Silicon isotopes; upper continental crust; shale; loess; MC-ICPMS

1. INTRODUCTION

Silicon (Si) is the second most common element in the Earth's crust (Wedepohl, 1995; Rudnick and Gao, 2003), and the upper continental crust (UCC) is the major source of primary silica to the oceans; around 85% of marine silica is derived from the continents (Tréguer et al., 1995). The (supracrustal) Si cycle is also intrinsically linked with the carbon cycle because it is a major nutrient for planktonic diatoms which represent ~40% of marine primary productivity (e.g. Tréguer et al., 1995; Hendry et al., 2010). These organisms with silica skeletons sequester carbon and hence mediate atmospheric CO₂ through burial (Ragueneau et al., 2000). In addition, weathering of silicate minerals through reaction with carbonic acid (dissolved in meteoric water) also provides a sink for atmospheric CO₂ (Walker et al., 1981). As stable isotope fractionation can provide information about sources and rates in such cycles, the Si isotope system is of obvious relevance to the aforementioned processes.

Over the last decade there have been a number of studies investigating Si isotopes in biological and weathering processes. These have demonstrated that isotopic fractionation is generated as a result of biological utilisation by marine organisms (De La Rocha et al., 1998; Hendry et al., 2010) or vegetation (Ding et al., 2005; Opfergelt et al., 2008; Bern et al., 2010), low-temperature weathering (Ziegler et al., 2005a&b; Georg et al., 2009a; Bern et al., 2010; Opfergelt et al., 2009, 2010, 2011, 2012; Steinhoefel et al., 2011) and precipitation of secondary silica (Basile-Doelsch et al., 2005). Precipitation of secondary minerals tends to enrich the product in the lighter isotopes of Si – compared to unweathered igneous rocks ($\sim -0.4 < \delta^{30}\text{Si} < -0.1\text{‰}$; Savage et al., 2010, 2011, 2012), large negative mineral enrichments of $\delta^{30}\text{Si} \approx -6.0$ to -3.0‰ have been deduced (e.g., Basile-Doelsch et al., 2005; Ziegler et al., 2005a&b) – resulting in a fluid with a relatively heavy isotopic composition (De la Rocha et al., 2000; Ding et al., 2004, Georg et al., 2006a, 2009b; Cardinal et al., 2010). This appears to be as a result of dynamic equilibrium between dissolution and re-precipitation of Si, whereby the degree of isotopic fractionation is much greater during the formation of secondary phases than during dissolution

62 (e.g. Ziegler et al., 2005a). There has, however, been no systematic study of the overall Si isotopic
63 composition of, and the degree of isotopic heterogeneity within, the continental crust. Ultimately, all Si
64 utilised in the above environments is sourced from the continents and so characterising this source is
65 essential.

66 The widely-cited studies of Douthitt (1982) and Ding et al. (1996) were the first to hint at the
67 isotopic composition of the continental crust but, since then, very little progress has been made. In both
68 studies it was demonstrated that evolved (high-Si) igneous rocks tended to be enriched in the heavier
69 isotopes of Si and were more isotopically variable when compared to basalts and mantle lithologies.
70 Such observations have since been reappraised using modern analytical techniques, but are still broadly
71 accepted (Savage et al., 2010, 2011, 2012). The earlier studies also suggest that chemically derived
72 sedimentary material (e.g., siltstone, shale) is, in general, isotopically lighter, whereas the Si isotopic
73 composition of mechanically derived sediment (e.g., sandstone) is comparable to that of igneous rocks
74 (again, these observations have been corroborated by more recent weathering studies, see above).
75 However, both of these studies were aimed at cataloguing the natural variation of Si isotopes, and no
76 attempt was made to provide an average isotopic composition for the UCC.

77 This research uses a well-characterised set of shale and loess samples, as well as the data for
78 granitoid material previously acquired (Savage et al., 2012) to characterise the UCC. The degree of Si
79 isotopic heterogeneity in the UCC is also constrained.

80

81 **2. SAMPLES**

82

83 **2.1 Loess**

84 Loess is aeolian sediment that covers approximately 10% of the world's land surface and is
85 deposited during cold-dry climatic phases (Taylor et al., 1983; Pye, 1995). It is composed mainly of
86 quartz, feldspar, sheet silicates and/or calcite depending on regional geology, and is derived

87 predominantly from deserts and/or glacial milling (Taylor et al., 1983). Mechanical sedimentary
88 derivation from glacial milling has limited the extent of chemical weathering that has affected loess,
89 although most loess has experienced at least one cycle of chemical alteration (Gallet et al., 1998).
90 Because loess samples large areas of crust, it has been used by many to constrain the average
91 composition of the upper continental crust (e.g., Taylor et al., 1983; Barth et al., 2000; Hu and Gao,
92 2008). We have analysed 13 Pleistocene loess samples, sourced from China, New Zealand, Germany,
93 Hungary and the USA, which have previously been studied for major and trace elements (Taylor et al.,
94 1983, Gallet et al., 1998, Barth et al., 2000; Hu and Gao, 2008) and Li and Mg stable isotopes (Teng et
95 al., 2004; Li et al., 2010). The major element composition of loess is somewhat variable, with each
96 suite reflecting the diverse regional geology of its source region, e.g., Si-rich loess from the Banks
97 Peninsula is derived from Mesozoic greywackes from the Southern Alps, whereas European loess is
98 more carbonate-rich, reflecting its derivation from Alpine terrains. The Iowa and Kansas loess is
99 thought to derive from the Rocky Mountains; by contrast, much Chinese loess is non-glacial, deriving
100 instead from a desert environment (Taylor et al., 1983).

101 Degree of chemical weathering of a sediment is often established using the Chemical Index of
102 Alteration (CIA; Nesbitt and Young, 1982) which is defined as $CIA = \text{molar } Al_2O_3 / [Al_2O_3 + CaO^* +$
103 $Na_2O + K_2O]$. In this equation, CaO^* refers to the CaO present only in silicates, not in apatite and
104 carbonate, and is corrected using molar P_2O_5 and Na_2O quantities (see McLennan, 1993). The loess
105 samples analysed in this study have CIA values between 57 and 65, which is slightly elevated when
106 compared to unweathered igneous rocks ($CIA \sim 50$; Nesbitt and Young, 1982), but lower than shales
107 (see later), consistent with the suggestion of Gallet et al. (1998) that most loess has experienced minor
108 chemical weathering.

109

110 **2.2 Shales**

111 Shales are fine-grained sedimentary rocks composed mainly of clay minerals, detrital quartz,

112 and variable amounts of carbonate, which are deposited in low energy environments. They are derived
113 from erosion over large areas and so, like loess, are often used as representative samples of the upper
114 continental crust (e.g., Haskin and Haskin, 1966; Nance and Taylor, 1976; Gromet et al., 1984; Taylor
115 and McLennan, 1985; Barth et al., 2000). Shale petrogenesis is more complicated than loess, involving
116 both mechanical and chemical weathering, as well as variable amounts of diagenesis and
117 metamorphism, resulting in higher CIA values than loess. Despite this, shales show little variation in
118 their insoluble element ratios (Taylor and McLennan, 1985) and so provide good estimates for these in
119 the upper crust. Also, whereas loess is normally confined to the Pleistocene, shales are present in the
120 geological record throughout most of Earth's history.

121 Thirty eight samples, taken from Australia, Canada and the USA were analysed for Si isotopes.
122 Twenty two shales were analysed from the Post-Archaean Australian Shale (PAAS) suite, originally
123 used by Nance and Taylor (1976) to estimate the rare earth element composition of the upper
124 continental crust, and subsequently by Taylor and McLennan (1985), Barth et al. (2000) and Hu and
125 Gao (2008) for further trace element work, and Teng et al. (2004) and Li et al. (2010) for Li and Mg
126 stable isotopes studies, respectively. These samples were collected from across Australia (see Figure 1
127 in Nance and Taylor, 1976) and span a wide range of ages from mid-Proterozoic (1.5 Ga) to Triassic
128 (200-250 Ma). All samples were taken from drill cores to avoid the effects of weathering and/or
129 leaching. CIA values of the PAAS shales are high and variable, ranging from 66 to 80 (c.f. ~50 for
130 unweathered igneous rocks). As well as the PAAS samples, we have analysed two shales from the
131 Pilbara Supergroup, Western Australia (McLennan et al., 1983), which have Archaean deposition ages
132 of 3.4 Ga (Gorge Creek) and 2.7 Ga (Whim Creek) respectively.

133 Seven samples were taken from the Huronian Supergroup and Sudbury Basin suites, Canada
134 (McLennan et al., 1979; McDaniel et al., 1994; McLennan et al., 2000). Samples from the Huronian
135 Supergroup are early Proterozoic in age and are composed predominantly of granitoid and volcano-
136 sedimentary material derived from the Archaean-age Superior Province (McLennan et al., 1979). A

137 slightly younger (1.85 Ga) sandstone from the nearby Sudbury basin (McDaniel et al., 1994), which is
138 again thought to derive from the Superior Province, was also analysed. Some of these samples
139 resemble tillites or glacial mudstones (i.e., the Gowganda samples, see Table 3) that have not
140 experienced large amounts of chemical alteration, as evinced by their lower CIA values. These samples
141 may therefore be more representative of unweathered Archaean continental crust, rather than the more
142 chemically altered shales.

143 Four metasedimentary samples were analysed from the Honda Group and Uncomphagre
144 Formation in south-western North America (McLennan et al., 1995). These samples represent a
145 quartzite-pelite stable-shelf succession, derived from differentiated Proterozoic-age crust with small but
146 variable amounts (10–25%) of Archaean material. The major element compositions indicate that these
147 samples contain minor carbonate and have undergone severe weathering before deposition (McLennan
148 et al., 1995).

149 Finally, the USGS shale standards SDO-1, SCo-1 and SGR-1b were also analysed. All of these
150 samples are from the USA and contain varying amounts of carbonate material, with SCo-1 showing the
151 strongest terrestrial affinity. Sample SGR-1b is from an oil shale, which has anomalously low SiO₂
152 content (< 30 wt. %) and CIA value (36), because this sample is not predominately silicate-derived.

153

154

3. METHODS

155

156 Samples were prepared for MC-ICPMS analysis following the methods and techniques detailed
157 by Georg et al. (2006b). These are comprehensively described in the aforementioned paper, and
158 elsewhere (e.g., Armytage et al., 2011; Savage et al., 2011; Zambardi and Poitrasson, 2011); as such,
159 only a brief summary and any sample-pertinent information will be provided here. All samples were
160 received as powders, some of which had been milled in agate. It has been demonstrated that this does
161 not cause resolvable contamination for Si isotope analysis (e.g., Savage et al., 2011; Zambardi and

162 Poitrasson, 2011).

163 Between 5 and 10 mg of sample powder was weighed into a silver crucible along with ~ 200 mg
164 of NaOH flux (analytical grade in pellet form). The crucible was then placed into a furnace, heated at
165 720°C for 12 minutes, then removed and allowed to cool slightly. After fusion, the crucible was placed
166 into 20 ml of MQ-e water in a Teflon beaker, and left to react for 24 hours. Afterwards, the beaker was
167 left in an ultrasonic bath (heated to ~ 60°C) for 20 minutes, then transferred from the crucible via a
168 pipette into pre-cleaned 125 ml PP bottles. Finally, the sample was diluted with MQ-e water and
169 acidified (1% v/v) with triple-distilled HNO₃. Sample yield was then checked using the “Heteropoly
170 Blue” method (whereby Si is measured in the form of a Mo-Si complex) using a Hach Lange DR 2800
171 photospectrometer. The average yield for all loess and shale samples processed in this study is $96 \pm 4 \%$
172 (2 s.d.).

173 Samples were quantitatively purified before MC-ICPMS analysis using a single-pass column
174 technique with strong cationic resin (BioRAD AG50W X12, 200-400 mesh, in H⁺ form). Silicon, at
175 neutral to low pH, exists in solution as either anionic or neutral species, so it is not retained by the
176 resin. It is therefore eluted immediately in MQ-e water, and all cations are quantitatively stripped from
177 the sample (Georg et al., 2006b). The samples were acidified after purification to 1% v/v HNO₃. All
178 samples and standards, including the bracketing standard, underwent identical chemical processing
179 before analysis, and the external standards BHVO-2 and Diatomite (see Section 4.1) were routinely
180 analysed to assess method accuracy and reproducibility.

181 There is some evidence that the presence of anionic species (e.g. organic carbon, SO₄²⁻, NO₃⁻) in
182 the eluant can lead to matrix effects on the measured Si isotopic ratios: both van den Boorn et al.
183 (2009) and Hughes et al. (2011) show that high SO₄²⁻/Si and C/Si ratios can cause substantial shifts in
184 the measured Si isotope composition of various rock standards, including BHVO-2 and SGR-1. Our
185 analyses of both of these standards are identical within error to the recommended, matrix-free, values
186 for these materials (see Table 1), even though we did not employ any further steps to combat matrix

187 effects. It is highly likely that the alkali fusion step, at 720°C, should act to volatilise and thus remove
188 much of the sulphate and carbon (Savage et al., 2010; Zambardi and Poitrasson, 2011); also it has also
189 been suggested that some MC-ICPMS instrumental setups may be more sensitive to matrix effects than
190 others (Hughes et al., 2011). Nevertheless, the good agreement between our external standard
191 measurements and those provided by van den Boorn et al. (2009) and Hughes et al. (2011) strongly
192 implies that our data are uncompromised by matrix-effects, even for samples such as SGR-1 which
193 have high $\text{SO}_4^{2-}/\text{Si}$ ratios.

194 Silicon isotope measurements were made at the University of Oxford on a Nu Instruments
195 (Wrexham, UK) Nu Plasma High Resolution Multi-Collector Inductively-Coupled-Plasma Mass
196 Spectrometer (HR-MC-ICPMS). The machine and running conditions are detailed in Belshaw et al.
197 (1998) and Georg et al. (2006b). The machine was operated at “medium” resolution (resolving power
198 $m/\Delta m \sim 3300$, where Δm is defined at 5% and 95% for peak height; Weyer and Schwieters, 2003) to
199 avoid poly-atomic interferences (e.g., $^{28}\text{Si}^1\text{H}^+$, $^{14}\text{N}^{16}\text{O}^+$) that would otherwise prevent the accurate
200 measurement of all three Si isotopes. This entails physically narrowing the ion beam and typically
201 results in a $\sim 85\%$ reduction of instrument sensitivity. During the course of this study, typical sample
202 run Si concentrations were between 750 ppb and 1.0 ppm (depending on machine conditions), which
203 gave a total signal of $\sim 1 \times 10^{-10}$ A and a signal to noise ratio of ~ 400 .

204 To correct for instrumental mass-bias, Si isotope values were calculated using the standard-
205 sample bracketing technique, with NBS28 (NIST RM8546) silica sand as the bracketing standard.
206 Isotopic variations from this standard are represented in per mil (‰) using the delta notation, defined
207 as:

208

$$\delta^{30}\text{Si} = [(^{30}\text{Si}/^{28}\text{Si}_{\text{sample}})/(^{30}\text{Si}/^{28}\text{Si}_{\text{standard}}) - 1] \times 1000;$$

210

$$\delta^{29}\text{Si} = [(^{29}\text{Si}/^{28}\text{Si}_{\text{sample}})/(^{29}\text{Si}/^{28}\text{Si}_{\text{standard}}) - 1] \times 1000.$$

211

212 We discuss our Si isotopic data using $\delta^{30}\text{Si}$ values, which are roughly twice the magnitude of $\delta^{29}\text{Si}$
213 values. Assuming mass dependence, which, for terrestrial samples, is a valid assumption, this
214 relationship was used as a further test for data quality, as unresolved isobaric interferences should result
215 in an artificially high abundance of one (or more) of the isotopes of interest.

216

217

4. RESULTS

218

219 4.1 External standards

220 The external standards Diatomite (a pure natural silica standard) and BHVO-2 (Hawaiian basalt,
221 USGS) were routinely analysed to assess sample data accuracy and precision. Both are widely
222 available and often utilised; as such, well-established literature data are available for comparison. Also
223 analysed was the USGS SGR-1b oil shale standard, which has also been analysed by Hughes et al.
224 (2011). External standard data are given in Table 1 as well as some reference values (Reynolds et al.,
225 2007; Abraham et al., 2008; Georg et al., 2009a; Hughes et al., 2011; Savage et al., 2011; Zambardi and
226 Poitrasson, 2011). The data for all standards are in excellent agreement with the literature data, and
227 illustrate the good levels of accuracy and reproducibility that our methods can attain. The external
228 reproducibility can be estimated by calculating the 2 s.d. ($2 \times$ the standard deviation) of the mean of the
229 individual standard analyses given in Table 1. The averages and 2 s.d. are as follows – Diatomite: $\delta^{30}\text{Si}$
230 $= 1.22 \pm 0.03 \text{ ‰}$; $n = 12$; BHVO-2: $\delta^{30}\text{Si} = -0.30 \pm 0.04 \text{ ‰}$; $n = 12$ – the largest of these values (\pm
231 0.04 ‰) is taken to represent the external reproducibility.

232 Silicon isotope data for the loess and shale samples are given in Tables 2 and 3, respectively.
233 Errors for individual sample analyses are represented by both 2 s.d. and 95% standard error of the
234 mean, calculated as such: $95\% \text{ s.e.} = t \times \text{s.d.}/(n)^{1/2}$, where t = inverse survival function of the Student's
235 t-test at the 95% significance level and $n-1$ degrees of freedom; the 95% s.e. values ($\pm 0.01 - 0.05 \text{ ‰}$;
236 $\text{mean} \pm 0.03 \text{ ‰}$), which are appropriate as one aliquot of each sample was analysed, are similar to our

237 external precision values calculated above.

238

239 4.2 Loess

240 Loess displays limited variation in Si isotopes, with $\delta^{30}\text{Si}$ values ranging from -0.28 to -0.15‰,
241 and an average value of $\delta^{30}\text{Si} = -0.22 \pm 0.07 \text{ ‰}$ (2 s.d., $n = 13$, Fig. 1). There is some minor isotopic
242 variation between localities, with the European (German and Hungarian) loess samples having slightly
243 heavier $\delta^{30}\text{Si}$. However, these variations are within error and there are no resolvable differences
244 between loess derived from distinct continental provinces. There are also no strong correlations with
245 SiO_2 content, weathering degree (CIA values) or other isotope systems (Figs. 2, 3b and 4). This limited
246 isotopic range is in contrast to the $\delta^{26}\text{Mg}$ and $\delta^7\text{Li}$ values of these samples, which display $3\times$ and $60\times$
247 greater isotopic variability, respectively (Teng et al., 2004; Li et al., 2010).

248

249 4.3 Shales

250 In contrast to the loess data, the PAAS samples define a wider range of $\delta^{30}\text{Si}$ values, with
251 samples ranging from $\delta^{30}\text{Si} = -0.80$ to 0.00 ‰ (average $\delta^{30}\text{Si} = -0.37 \pm 0.47 \text{ ‰}$; 2 s.d., $n = 22$; 2 s.d. is
252 abnormally large because the data are not normally distributed). Compared to igneous rocks ($\sim -0.4 <$
253 $\delta^{30}\text{Si} < -0.1\text{‰}$; Savage et al., 2010, 2011, 2012), this is a wide spread of Si isotope compositions
254 although it is somewhat limited compared to the much larger isotope variations measured in secondary
255 minerals and soils ($\sim -6.0 < \delta^{30}\text{Si} < +1.0 \text{ ‰}$; e.g. Basile-Doelsch et al., 2005; Ziegler et al., 2005a&b;
256 Opfergelt et al., 2010, 2011, 2012). Within each locality (with the exception of the Mt. Isa shales) there
257 is remarkably limited Si isotope variation. There are no strong correlations between Si isotopes and
258 SiO_2 (Fig. 2) or Li and Mg stable isotope compositions (Fig. 4), although there is a scattered negative
259 trend ($R^2 = 0.14$) with CIA values (Fig. 3a). The two Archaean-age Pilbara shales from Australia are
260 both isotopically much lighter than igneous rocks (sample Pg-7 displays the lightest $\delta^{30}\text{Si}$ value
261 analysed in this study, viz. $-0.82 \pm 0.04 \text{ ‰}$, 95% s.e.), and show similar isotopic compositions to some

262 of the younger PAAS samples. The data for the SW USA shales (Honda and Uncomphagre) also show
263 a limited range ($\delta^{30}\text{Si} = -0.51$ to -0.40 ‰, average $\delta^{30}\text{Si} = -0.47 \pm 0.10$ ‰; 2 s.d., $n = 4$), again lighter
264 than the range for igneous rocks.

265 Silicon isotope data for the Canadian samples (Huronian and Sudbury) range from $\delta^{30}\text{Si} = -0.41$
266 to -0.16 ‰ (average $\delta^{30}\text{Si} = -0.25 \pm 0.20$ ‰; 2 s.d., $n = 7$). The range of Si isotopic compositions is
267 smaller than for the PAAS samples, with the data falling into two populations; one near $\delta^{30}\text{Si} = -$
268 0.39 ‰, the other around $\delta^{30}\text{Si} = -0.19$ ‰, the possible causes of which will be discussed later.

269 The USGS standards are geologically unrelated, with varied petrogenetic histories and ages.
270 The $\delta^{30}\text{Si}$ data lie within the range defined by PAAS shales. Sample SGR-1b, an organic-rich oil-shale,
271 has a relatively heavy Si isotopic composition ($\delta^{30}\text{Si} = +0.01 \pm 0.04$ ‰, 2 s.d.); this could indicate the
272 presence of biogenic silica, which is typically isotopically heavy compared to terrestrial silicate
273 material (e.g., De la Rocha et al., 1998; Opfergelt et al., 2008; Hendry et al., 2010).

274

275 5. DISCUSSION

276

277 The data described above show that, with respect to Si isotopes, the UCC is heterogeneous
278 relative to the mantle and igneous rocks (Savage et al., 2010, 2011, 2012). The following discussion
279 concerns how these data can be used to constrain the Si isotopic composition of the modern day UCC,
280 as well as interpreting the Si isotope composition of clastic sedimentary material in terms of what is
281 already known about possible sources and Si isotope fractionation as a result of low temperature,
282 critical zone, processes. These results will then be combined with data from other sources to calculate
283 an average UCC Si isotopic composition.

284

285 5.1 Loess as a proxy for the composition of the UCC

286 The differences in isotopic heterogeneity between loess and shales reflect the different

287 petrogenetic histories of these two lithologies. The consistency of the Si isotopic composition of loess
288 from all over the globe is remarkable. Not only is the range of loess $\delta^{30}\text{Si}$ limited with respect to shale
289 samples, it is also smaller than the isotopic range displayed by igneous rocks (Fig. 1). This is despite
290 loess sampling a wide range of lithologies (Taylor et al., 1983), exhibiting a broad range of chemical
291 compositions (SiO_2 content ranging from 52 to 81 wt.%, with the high SiO_2 in some loess reflecting
292 concentration of quartz; Fig 2), and having, in general, experienced at least one cycle of chemical
293 weathering (Gallet et al., 1998). Finally, these same loess samples show resolvable (and in some cases,
294 quite large) variations in their $\delta^7\text{Li}$ and $\delta^{26}\text{Mg}$ values, which in both cases are related to weathering
295 processes (Fig. 4; Teng et al., 2004; Li et al., 2010). Why then, is the Si isotopic composition of loess
296 so consistent, when chemical weathering has been shown to generate resolvable Si isotopic
297 fractionation?

298 The most likely explanation for this can be found by taking into account the mineralogy of
299 loess, in which the most common Si-bearing phases are quartz and feldspar, i.e., primary igneous
300 minerals (Pye, 1995). Even though loess has undergone weathering, Si isotopes should only be affected
301 if there has been significant formation of secondary mineral phases. This is not so for the CIA value,
302 which is a proxy for loss of fluid-mobile elements (Ca, Na and K) with respect to Al, predominantly
303 due to breakdown of primary feldspar. Even though Si is more water-soluble than Al (at acidic to
304 neutral conditions; $2 < \text{pH} < 8$), it is much less so than Ca, Na and K (Turner et al., 1980) and increases
305 in CIA value recorded by loess should not necessarily imply any significant Si loss from the bulk rock.
306 On the other hand, Mg and Li isotopes are a) both strongly fluid mobile and b) not present in large
307 amounts in either quartz or feldspar, and are therefore more amenable to secondary weathering effects.

308 The average Si isotope value for loess is $\delta^{30}\text{Si} = -0.22 \pm 0.07 \text{ ‰}$ (2 s.d., $n = 13$). The major Si-
309 bearing phases in loess are quartz and feldspar, therefore loess is likely behaving as a proxy for the
310 composition of average quartz and feldspar in the UCC. We refer to this as “fresh crystalline” UCC and
311 it is identical to the average value for granites ($\delta^{30}\text{Si} = -0.23 \pm 0.15 \text{ ‰}$; 2 s.d.; Savage et al., 2012) and

312 also the average “igneous” value for the continental crust, calculated from the empirical igneous array
313 in Savage et al. (2011; $\delta^{30}\text{Si} = -0.23 \pm 0.05 \text{ ‰}$; 2 s.e. of the regression statistics).

314 The Canadian (Huronian and Sudbury) sediments define two Si isotope populations (Fig. 1),
315 which appear to be related to weathering degree, with the more isotopically negative group displaying
316 higher CIA values (Fig. 3). The samples with heavier Si isotopic compositions have CIA values
317 comparable to loess (Fig. 3b) and are thought to be glaciogenic (McLennan et al., 1979), i.e., they
318 formed via predominantly mechanical processes, similar to loess. If loess is taken to represent the Si
319 isotopic composition of crystalline modern day continental crust, then the low-CIA samples from the
320 Huronian and Sudbury basins should record the same reservoir at the time given by their deposition
321 ages, in this case between 2.2 and 2.5 Ga (McLennan et al., 2000). The average Si isotope composition
322 for these samples is $\delta^{30}\text{Si} = -0.19 \pm 0.05 \text{ ‰}$ (2 s.d.), identical within error to that given by modern day
323 loess ($\delta^{30}\text{Si} = -0.22 \pm 0.07 \text{ ‰}$). This is good, if modest, evidence that the Si isotopic composition of
324 crystalline upper continental crust has remained constant since at least 2.5 Ga. It is, however, difficult
325 to place conclusive limits on the basis of six samples from two localities, and it is not clear whether a
326 different melting regime at subduction zones before ca. 2.5. Ga (e.g., Taylor and McLennan, 1985;
327 Martin, 1986; Kemp and Hawkesworth, 2003) might have affected the Si isotopic composition of bulk
328 continental crust formed at this time.

329 The more isotopically negative shale samples from the Canadian suite, the Pilbara suite and
330 from SW USA are all derived from Archaean or Palaeo-proterozoic terrains, and were also deposited
331 during these geological periods. This implies that the UCC was as heterogeneous then, with respect to
332 Si isotopes, as it is today.

333

334 **5.2 The formation of shales**

335 If loess represents the average Si isotopic composition of the crystalline UCC, then the more
336 variable isotopic compositions in shales illustrate the effect that geological processes at the Earth's

337 surface have on Si isotopes, in particular, weathering and the sedimentary cycle. The effect of
338 weathering on Si isotopes is now well established, through studies of natural soil and clay formation as
339 well as studies of riverine Si and associated bedrock (Section 1) as well as some experimental work
340 (Ziegler et al, 2005a; Delstanche et al., 2009). These studies have established that precipitation of Si
341 from solution enriches the product (e.g., secondary mineral phases) in the light isotopes of Si, leaving
342 an isotopically heavy fluid.

343 Given that shales are composed of significant quantities of clay minerals, do the Si isotopic
344 compositions of shales reflect their mineralogy? Certainly, some samples do display light $\delta^{30}\text{Si}$ values
345 (i.e., Perth Basin, Pilbara) and the mean $\delta^{30}\text{Si}$ value for shales is lighter than for loess. However, there
346 are some shales that have $\delta^{30}\text{Si}$ values that are similar to igneous material and, also, some samples that
347 display Si isotopic compositions that are *heavier* than unweathered continental crust (i.e., the Mt. Isa
348 group). Also, given the large (per mil) enrichments in light Si isotopes recorded in many secondary
349 phases, particularly in clay minerals (e.g. Opfergelt et al., 2012), it is somewhat surprising that the Si
350 isotopic variations recorded in shales are limited to the sub-per mil scale.

351 It appears that the presence of secondary phases does not always cause a shift towards light Si
352 isotope compositions in shales. The poor relationships between $\delta^{30}\text{Si}$ and CIA values (Fig. 3a) and Li
353 and Mg isotopic compositions (Fig. 4) might serve to illustrate this; however, as noted for the loess
354 samples, these quantities are not indicative of Si mobility during weathering. This is due to, in part, the
355 lower fluid mobility of Si compared to Li, Mg, Ca etc., and also the fact that Si is present in significant
356 quantities in both primary and secondary silicate minerals – therefore, the $\delta^{30}\text{Si}$ of a shale is likely
357 strongly controlled by the relative abundances of these two mineral groups, which in turn depends on
358 the degree of weathering a sedimentary source has undergone.

359 Weathering of upper crustal material can be divided into three stages (Chesworth, 1977;
360 Kronberg et al., 1979). “Early stage” weathered material is dominated by primary minerals (that is,
361 minerals that constitute fresh igneous or metamorphic lithologies) with a clay fraction consisting of

362 chlorite, vermiculite, smectite and illite. Loess is a good example of “early stage” weathering (e.g. Pye,
363 1995). “Intermediate stage” weathered material typically contains detrital quartz and a clay fraction
364 predominately composed of smectite and illite (2:1 clays – one octahedral hydroxide “sheet” per two
365 tetrahedral silicate “sheets”), accompanied by loss of feldspar. “Late stage” material is dominated by
366 the quartz-kaolinite (1:1 clays – one hydroxide to one silicate “sheet”)–gibbsite-goethite assemblages.

367 Shales typically have intermediate to late-stage mineralogies, where feldspar has been
368 completely replaced by clay minerals but detrital quartz is still modally significant. Clay minerals are
369 isotopically much lighter than primary feldspars but quartz will have a heavier Si isotopic composition,
370 which will serve to dilute the strongly fractionated clay mineral signature, depending on the detrital
371 quartz abundance. Also, the type of clay minerals present in the shale is likely to exert a control on the
372 bulk Si isotope composition: there is now strong evidence that formation of more mature (more
373 desilicified) 1:1 clays is accompanied by much larger degrees of Si isotopic fractionation than 2:1
374 clays, with kaolinite displaying the most negative $\delta^{30}\text{Si}$ values (Georg et al., 2009a; Opfergelt et al.,
375 2012). During “late stage” alteration, an isotopic shift to lighter values associated with kaolinite
376 formation could also be compounded by the associated formation of Fe oxides, as sorption of Si on to
377 Fe-oxides also results in an enrichment of light Si isotopes (Delstanche et al., 2009; Opfergelt et al.,
378 2009). Therefore, quantifying the amount of primary Si remaining (that is, the amount of
379 desilicification that a shale has undergone) as well as the variety of clay minerals present may be more
380 useful for quantifying shale Si isotopic compositions.

381 One way to assess this is to study the relationship between Si isotopes and Al/Si ratios, and
382 insoluble element concentrations, such as the rare earth elements (REEs), Nb, Ti, etc. An increased
383 abundance of 1:1 clays in a sample should correspond to a higher Al/Si ratio, and also, because of
384 progressive chemical denudation, insoluble element concentrations (Duddy, 1980). Laterite formation,
385 for example, which involves intense degrees of weathering, can significantly concentrate the REEs
386 (Kronberg et al., 1979) and would be predicted to result in light Si isotope compositions, due to the

387 significant abundances of kaolinite and Fe-oxides in laterites. It is striking, therefore, that negative
388 correlations do exist between Si isotope composition and Al/Si ratios as well as insoluble element
389 concentrations in shales, for instance TiO_2 ($R^2 = 0.41$), Ho ($R^2 = 0.45$), Hf ($R^2 = 0.55$ – not including
390 loess, which show evidence of zircon accumulation; Taylor et al., 1983). The examples of Al/Si and
391 Nb are shown in Figure 5. These relationships indicate that the shales that display the largest
392 enrichment in Al/Si ratios (i.e. have higher kaolinite abundances) and insoluble elements (i.e., have the
393 lowest Si_{qtz} contents) tend to have the lightest Si isotope compositions compared to igneous crust (e.g.,
394 Pilbara, Perth Basin). Those shales with Al/Si and insoluble element compositions close to average
395 upper crust also have Si isotope compositions similar to igneous upper crust (e.g., State Circle). All
396 shales show similar depletions of fluid-mobile elements as a result of feldspar breakdown (recorded by
397 their CIA values), but in samples enriched in the insoluble elements, alteration has been more intense or
398 involved reworking of already-weathered sediment – enough to induce negative shifts in Si isotope
399 composition. Another outcome of the relationship between Si isotopes and insoluble element
400 concentrations is that it offers a possible explanation for the relatively heavy Si isotopic compositions
401 in some shales. Taylor and McLennan (1985) noted that shales with low REE content contain a
402 significant quantity of marine-derived material. The concentration of rare earth elements in seawater is
403 low because they are extremely particle reactive, so are removed from the water column by scavenging
404 (e.g. Elderfield, 1988; Halliday et al., 1992). This is reflected in the REE content of carbonates and
405 other marine lithologies, including cherts and siliceous ooze. Seawater also has a heavy Si isotope
406 composition (De La Rocha et al., 2000), and so seawater derived authigenic silica is also relatively
407 heavy, compared to igneous rocks (De la Rocha et al., 1998; Hendry et al., 2010; also cf. Diatomite
408 standard). Therefore, if a sediment is predominantly marine, then it will have low insoluble element
409 concentrations, low Al/Si ratios and heavy Si isotope compositions, which can explain the deviation
410 toward heavier Si isotopes in Figure 5. In this regard, it is worth noting that the isotopically heavy Mt.
411 Isa Group has chert, dolomite and carbonate horizons and contains stromatolites and halite

412 pseudomorphs (Geoscience Australia; <http://dbforms.ga.gov.au>).

413 An important aspect to stress is that the processes that control the Si isotopic composition of
414 shales, namely intensive weathering and addition of marine-derived silica, are not mutually exclusive.
415 Mixing between these two end-members could result in a Si isotopic composition that is unfractionated
416 with respect to igneous rocks, masking the various isotopically fractionated components of such a
417 sample

418 This is illustrated in Figure 6, where we have modelled the various sedimentary components
419 and processes in shales (and loess), in terms of their $\delta^{30}\text{Si}$ and Al/Si values. The starting material is
420 granitic, composed of 60% feldspar ($\delta^{30}\text{Si} = -0.30\text{‰}$) and 40% quartz ($\delta^{30}\text{Si} = -0.20\text{‰}$; mineral $\delta^{30}\text{Si}$
421 based on analyses in Savage et al., 2012), which gives an initial composition of $\delta^{30}\text{Si} = -0.25\text{‰}$, Al/Si =
422 0.25 (star symbol in Fig. 6). The simplest scenario in Figure 6 is feldspar dissolution, or quartz
423 accumulation, illustrated by line A. This lowers the Al/Si ratio but barely affects $\delta^{30}\text{Si}$, and fits the loess
424 data well, illustrating the strong control that primary igneous minerals have on the Si isotope
425 composition of loess (Section 5.1).

426 Scenarios B and C in Figure 6 both illustrate secondary mineral formation, whereby feldspar is
427 gradually replaced by 2:1 smectite clay ($\delta^{30}\text{Si} = -1.1\text{‰}$, Al/Si = 0.67) or 1:1 kaolinite clay ($\delta^{30}\text{Si} = -$
428 2.0‰ , Al/Si = 1; clay mineral $\delta^{30}\text{Si}$ taken from Opfergelt et al., 2012). In both scenarios there is also a
429 reduction in the abundance of detrital quartz. Where smectite is replacing feldspar and there has been
430 25% reduction of detrital quartz (scenario B), the most negative predicted value is $\delta^{30}\text{Si} = -0.63\text{‰}$.
431 Whilst this minimum can account for many of the shale Si isotope compositions, it fails to model many
432 of the Al/Si ratios well. Scenario C, in which kaolinite is forming at the expense of feldspar, and there
433 is a much large (60%) remobilisation of detrital quartz, fits the shale data to a better degree. In this
434 instance, the most negative shale samples can be explained by 70% replacement of the feldspar by
435 clays, and a loss of ~45% of the original quartz; in other words, these shales have
436 quartz:feldspar:kaolinite abundances of ~ 0.3:0.2:0.5. In reality it is unlikely that feldspar is present at

all in shale, but this serves to illustrate that kaolinite appears to be an important phase in creating the lightest Si isotope compositions in shales. It is also highly unlikely that a shale will be sourced from a single lithology and this is illustrated by the horizontal deviations from the linear array in Figure 6; an offset towards lower Al/Si implies accumulation of quartz, an offset toward higher Al/Si implies accumulation of clay minerals.

A final component in the system is that of authigenic marine silica, as shown by scenario D. This describes simple mixing between the granitic starting composition and the Diatomite standard ($\delta^{30}\text{Si} = +1.24\text{‰}$, Al/Si = 0) and shows that, for example, only ~10% incorporation of this highly fractionated material is needed to explain the heavier Si isotope compositions of the Mt. Isa group shales. This could be a conservative estimate, as Diatomite is by no means the most fractionated authigenic material measured in the literature, with some stromatolitic samples display Si isotope compositions of $> 3\text{‰}$ (Hendry et al., 2010; Wille et al., 2010). This also assumes that the starting material is unweathered – a shale with both high kaolinite and biogenic silica content could have a loess-like Si isotope composition, because weathering and addition of biogenic silica are antithetic (and sub-parallel, see Fig. 6). Other proxies are required to tease out the relative contributions of terrestrial and authigenic marine silica to a shale if, for instance, negative Si isotope deviations from “igneous” were to be used as a proxy for degree of large-scale terrestrial weathering. One possibility could be the use of Ge/Si ratios which are markedly different between biogenic and secondary silicate phases (e.g. Derry et al., 2005; Cornelis et al., 2011), but the Ge data for the samples used in this study, if present, are of too poor precision to infer any relationship.

It is clear that the Si isotope composition of shales is both source and process-related. Although it is very difficult to identify one major control, it appears that the balance of primary vs. secondary minerals (in particular, detrital quartz and kaolinite) is important. This degree of homogenisation is the reason why shales have been so useful, in previous studies, for constraining average UCC, and should provide a more representative upper crustal Si isotopic composition.

462

463 **5.3 The silicon isotope composition of the upper continental crust**

464 The upper continental crust consists predominantly of sedimentary and felsic igneous
465 lithologies (or their metamorphosed analogues; Wedepohl, 1995) and so by combining the data
466 acquired during this study with that for granitoid material (Savage et al., 2012), one may characterise
467 the Si isotopic composition of the UCC. These data are shown in histogram form in Figure 7. The
468 distribution is non-Gaussian when the shales are included, which reflects the greater variability and
469 more stochastic nature of the shale Si isotope compositions. A fairly sharp peak is centred around $\delta^{30}\text{Si}$
470 ~ -0.25 to -0.20 ‰ and is defined primarily by the granite and loess data, with the shale data defining
471 much larger and relatively even spread of Si isotope compositions.

472 The UCC is much more heterogeneous than the mantle or oceanic crust, with respect to Si
473 isotopes (Fig. 1). This heterogeneity is displayed by the shale samples, which reflect long-term and/or
474 intense chemical weathering processes, and also, the presence of marine-derived sedimentary material
475 that is now part of the continental crust. The granites define a more reduced range, but do show more
476 variability than their extrusive counterparts (rhyolites and dacites samples that show no evidence for an
477 evolved source during petrogenesis; Savage et al., 2011), likely to be the result of sediment anatexis
478 during granite petrogenesis (Savage et al., 2012). The loess define the narrowest range of Si isotopic
479 compositions, likely due to the fact that loess mineralogy is dominated by primary igneous silicates
480 (see Section 5.1). The overriding “igneous” affinity of loess is demonstrated by the fact that the average
481 value for loess ($\delta^{30}\text{Si} = -0.22 \pm 0.07$ ‰) is identical to that of granites ($\delta^{30}\text{Si} = -0.23 \pm 0.15$ ‰) and
482 indicates that the average loess value is a good proxy for the Si isotope composition of fresh crystalline
483 upper continental crust.

484 A more robust isotopic average for the upper continental crust requires an estimate of the
485 average proportions and SiO_2 compositions of the various lithologies that comprise the UCC. Using the
486 study of Wedepohl (1995), four major units can be defined, along with their average SiO_2 contents as

487 follows (Table 4): sedimentary lithologies (14%; $\text{SiO}_2 = 52.4$ wt.%); felsic intrusive lithologies (50%;
488 $\text{SiO}_2 = 69.2$ wt.%); gabbros (6%; $\text{SiO}_2 = 50.1$ wt.%); metamorphic lithologies (30%; $\text{SiO}_2 = 63.7$
489 wt.%). The average $\delta^{30}\text{Si}$ value for each of these units can then be calculated and used to derive a
490 weighted UCC Si isotopic composition. Note that the estimates of Wedepohl (1995) give a UCC SiO_2
491 content of 64.1 wt.%; this value has been superseded by a slightly higher value of 66.6 wt.% (Rudnick
492 and Gao, 2003), but recasting the data using this estimate does not affect the final outcome of the
493 calculation. In the following discussion, all errors are quoted to 2 s.d.

494 Using data from previous work, the granite average of $\delta^{30}\text{Si} = -0.23 \pm 0.15$ ‰ (Savage et al.,
495 2012) is used as an estimate for felsic volcanic rock, and, because there is insignificant Si isotopic
496 variation in mantle-derived igneous rocks (Savage et al., 2010), the BSE value of $\delta^{30}\text{Si} = -0.29 \pm$
497 0.08 ‰ is used to represent gabbro.

498 The greater degree of isotopic heterogeneity means that calculating a meaningful and reliable
499 average $\delta^{30}\text{Si}$ value for the sedimentary unit is more complicated. Firstly, four sub-units are defined
500 (shales and siltstones, sandstones, mafic volcano-clastic sediments and carbonates; Table 4), again
501 following the study of Wedepohl (1995). Silica contents of the sub-units are then calculated using the
502 SiO_2 averages of the samples analysed in this study, or, in the case of mafic volcano-clastic sediments
503 and carbonates sub-units, estimated from other studies. This approach yields an average unit
504 composition of $\text{SiO}_2 = 52.6$ wt.%, which is almost identical to that given by Wedepohl (1995). The
505 average $\delta^{30}\text{Si}$ value of all the shale samples analysed in this study is -0.36 ± 0.44 ‰, and this value was
506 used to represent the shale and siltstone sub-unit. The average loess $\delta^{30}\text{Si}$ value of -0.22 ± 0.07 ‰ is
507 used to represent the sandstone sub-unit because they are mineralogically similar, at least in terms of
508 the major Si-hosting phases. The BSE average is used to represent mafic volcanoclastic sedimentary
509 material, as with the gabbro unit. The carbonates were assumed to contain negligible amounts of Si,
510 and so are disregarded in the calculation (the final sedimentary $\delta^{30}\text{Si}$ value does not alter significantly
511 even if the carbonate unit were to contain 10 wt.% SiO_2 with a $\delta^{30}\text{Si}$ value of $+1.00$ ‰, due to the small

512 relative proportion of this unit). The above approach yields an average sedimentary unit $\delta^{30}\text{Si}$ value of -
513 0.31 ± 0.26 ‰.

514 To calculate an average $\delta^{30}\text{Si}$ value for the metamorphic unit, it is first assumed that this unit
515 contains lithologies that have protoliths present in similar proportions to those in the unmetamorphosed
516 portion of the upper continental crust, because the average SiO_2 composition of this unit is very similar
517 to that of the UCC (Table 4). Metamorphism does not appear to affect the bulk Si isotopic composition
518 of a sample (André et al., 2006), such that the $\delta^{30}\text{Si}$ value of this unit should be the weighted average of
519 the sedimentary, felsic and gabbroic units. Alternatively, removing the metamorphic unit from the
520 equation will not affect the final UCC $\delta^{30}\text{Si}$ value.

521 Using the above estimates, the average Si isotopic value of the upper continental crust is
522 calculated to be $\delta^{30}\text{Si} = -0.25 \pm 0.16$ ‰ (2 s.d. propagated error from the isotope compositions only;
523 including uncertainties associated with lithological unit abundances and their respective Si contents
524 does not introduce further significant uncertainty). This value coincides with the peak illustrated in
525 Figure 7. Strikingly, this value is only slightly heavier than, but within error of, the value for BSE.
526 Given that chemical weathering fractionates Si isotopes to a relatively large degree, this similarity is
527 perhaps surprising, but is easily explained by the fact that shales and siltstones comprise ~6 wt.% of the
528 UCC, such that these larger variations are effectively masked by the more abundant igneous material
529 (Wedepohl, 1995). The slight overall enrichment in heavier Si isotopes relative to BSE reflects the
530 predominance of felsic lithologies in the upper crust, which have relatively heavier Si isotopic
531 compositions. However, despite the larger spread of data for the UCC relative to BSE, these
532 compositions are identical within uncertainty, which reflects the competing nature of the different
533 sources of Si: igneous differentiation causes a slight enrichment in the heavy Si isotopes, but chemical
534 weathering counteracts this by readily enriching secondary minerals in the lighter isotopes.
535 Furthermore, addition of marine-derived, authigenic, silica to clastic sediments through orogenesis
536 introduces a heavy Si isotope source, which was previously released from the continents via chemical

537 weathering.

538

539

6. CONCLUSIONS

540

541 Pleistocene loess samples define a narrow range of Si isotopic compositions ($\delta^{30}\text{Si} = -0.28$ to -
542 0.15 ‰), a result of their primary igneous mineralogy and predominantly mechanical weathering
543 history, coupled with the averaging inherent in glaciogenic sampling. The average Si isotopic
544 composition of loess is $\delta^{30}\text{Si} = -0.22 \pm 0.07\text{ ‰}$ (2 s.d.), which is identical to the average Si isotope
545 composition of granites (Savage et al., 2012), and also the $\delta^{30}\text{Si}$ value calculated for continental crust
546 using the “igneous array” (Savage et al., 2011). This suggests that loess represents the Si isotopic
547 composition of fresh (crystalline) continental crust.

548 Compared to loess, the Si isotopic compositions of shales are much more variable ($\delta^{30}\text{Si} = -0.82$
549 to $+0.00\text{ ‰}$) which is a result of a more complicated petrogenesis that can involve, for instance,
550 chemical and physical weathering, diagenesis, etc. as well as variable source lithologies. The average
551 Si isotopic composition of shale ($\delta^{30}\text{Si} = -0.36 \pm 0.44\text{ ‰}$; 2 s.d.) is lighter than loess, due to increased
552 secondary mineral content.

553 Shales are not always isotopically light compared to unweathered igneous material, despite the
554 presence of secondary phases, and Si isotopes in shales do not correlate well with the canonical proxies
555 for weathering, such as CIA values. Instead, good negative correlations between $\delta^{30}\text{Si}$ values and Al/Si
556 ratios, insoluble element concentrations indicate that more intensive or prolonged chemical weathering
557 of a sedimentary source is required before resolvable negative Si isotopic fractionation occurs. In the
558 absence of marine-derived silica, the $\delta^{30}\text{Si}$ of a shale sample is a function of the abundance of detrital
559 quartz and the abundance and Si isotopic composition of the secondary phases in that sample. Heavy Si
560 isotopic compositions in shales relative to igneous rocks most likely indicate the presence of marine-
561 derived silica, either by reworking of marine lithologies or deposition in a marine environment.

562 The upper continental crust is heterogeneous with respect to Si isotopes ($\delta^{30}\text{Si} = -0.82$ to
563 $+0.00$ ‰) and has a weighted average composition of $\delta^{30}\text{Si} = -0.25 \pm 0.16$ ‰ (2 s.d.), which is only
564 slightly heavier than, but statistically identical to, the Bulk Silicate Earth.

565

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FIGURE CAPTIONS

Figure 1: Plot of $\delta^{30}\text{Si}$ values for the loess and shale samples analysed in this study (error bars are 95% s.e.), showing that loess is relatively homogeneous, and that shales define a large range of Si isotopic compositions. Also shown are $\delta^{30}\text{Si}$ values for I-, A- and S-type granites (Savage et al., 2012), extrusive igneous rocks (Savage et al., 2011) and Bulk Silicate Earth (Savage et al., 2010) for comparison.

Figure 2: Graph of $\delta^{30}\text{Si}$ against SiO_2 for all loess and shale samples (error bars are 95% s.e.) - see text for discussion. BSE value ($\delta^{30}\text{Si} = -0.29\text{‰}$) is taken from Savage et al (2010); granite average ($\delta^{30}\text{Si} = -0.23\text{‰}$; grey box $\pm 0.15\text{‰}$ 2 s.d.) is taken from Savage et al. (2012).

Figure 3: Graph of $\delta^{30}\text{Si}$ against CIA value for a) all shale samples and b) all loess samples (error bars are 95% s.e.). The CIA value is defined as $\text{CIA} = \text{molar Al}_2\text{O}_3 / [\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}]$, where CaO^* refers to the CaO present only in silicates (Nesbitt and Young, 1982, McLennan, 1993). BSE value ($\delta^{30}\text{Si} = -0.29\text{‰}$) is taken from Savage et al (2010); granite average ($\delta^{30}\text{Si} = -0.23\text{‰}$; dark grey box $\pm 0.15\text{‰}$ 2 s.d.) is taken from Savage et al. (2012). The light grey bar illustrates the range of CIA values for unweathered igneous material (50 ± 5 ; Nesbitt and Young, 1982). For the shale samples, a very vague negative trend exists between $\delta^{30}\text{Si}$ and CIA value ($R^2 = 0.14$), indicating a component of chemical weathering in the Si isotopic compositions of shales. No such relationship exists for loess. The Canadian samples have been plotted in both figures because the sample group contains both loess-like and shale-like samples.

Figure 4: Graph of $\delta^{30}\text{Si}$ against a) $\delta^7\text{Li}$ and b) $\delta^{26}\text{Mg}$ for the loess and shale samples, where available (error bars are 95% s.e.), which illustrates the large range of $\delta^{26}\text{Mg}$ and $\delta^7\text{Li}$ and small range of $\delta^{30}\text{Si}$ for the loess. Even though all three isotope systems are affected by weathering processes, there are no

771 strong relationships shown by the data.

772

773 **Figure 5:** Graph of $\delta^{30}\text{Si}$ against a) Al/Si ratio and b) Nb contents for loess and shales (symbols as in
774 Figure 3, error bars are 95% s.e.), which illustrates the good negative relationship between the two
775 (regression statistics calculated in Gnumeric; <http://projects.gnome.org/gnumeric/>). The average Al/Si
776 and Nb UCC compositions are taken from Rudnick and Gao (2003) and Barth et al., (2000); these
777 values correspond well to the average Si isotope loess composition. Similarly strong relationships exist
778 between $\delta^{30}\text{Si}$ and other insoluble elements; see text for discussion.

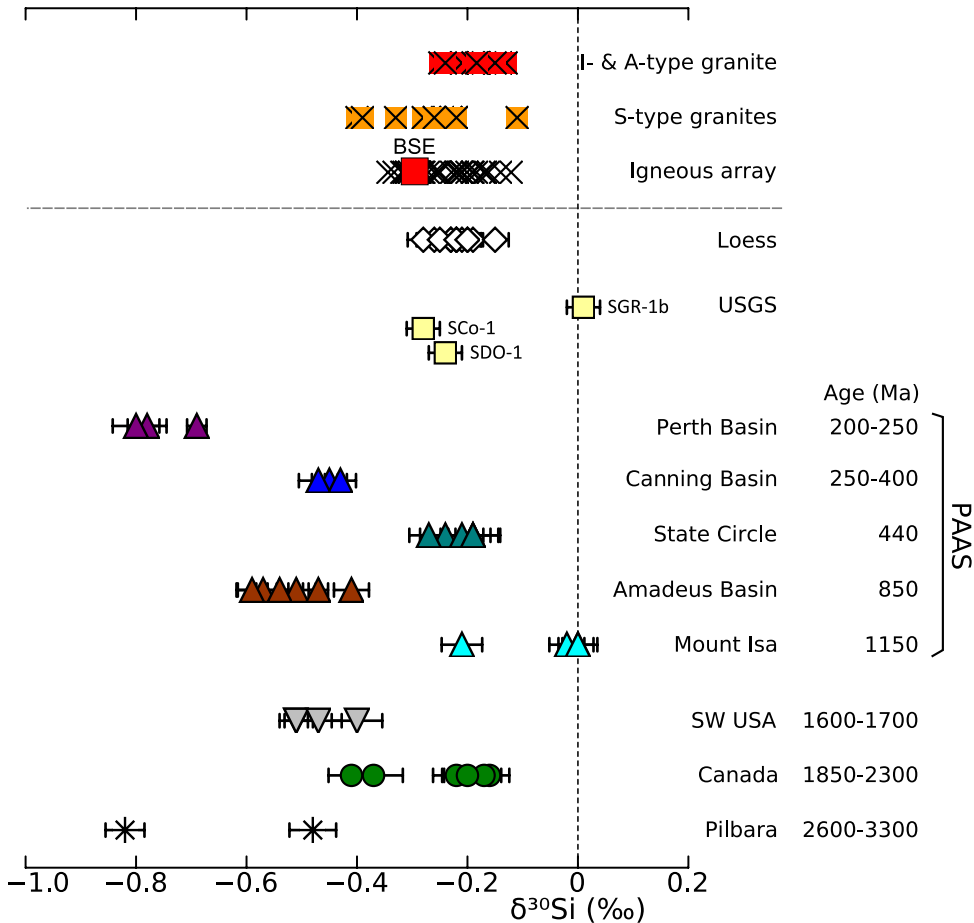
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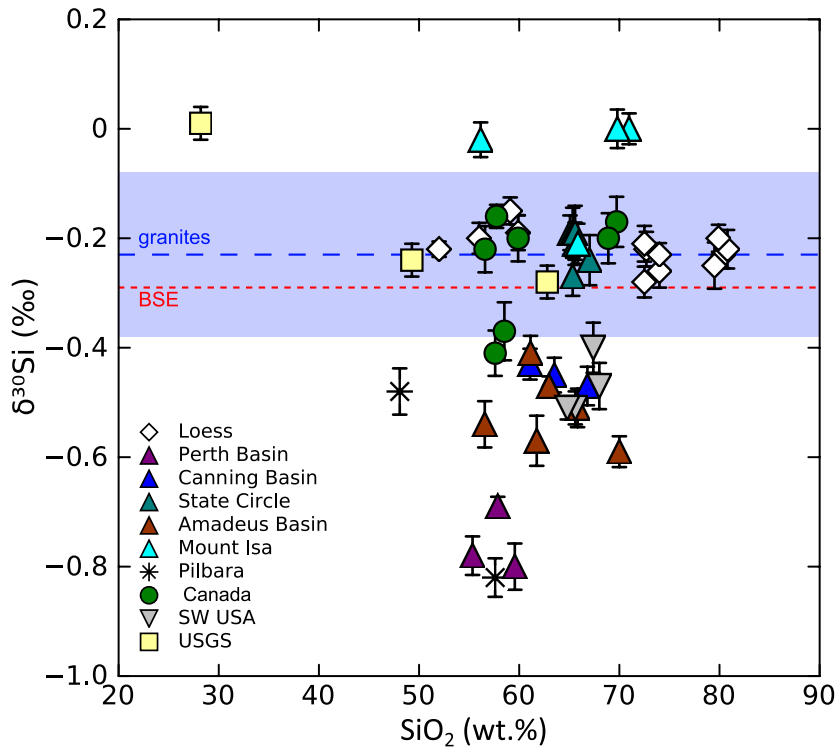
780 **Figure 6:** Modelled $\delta^{30}\text{Si}$ and Al/Si evolution of a putative “granite” starting composition (hereafter
781 “SC”, star symbol) along various weathering and mixing trajectories (tick marks along each line are
782 10%). Shale and loess data are also plotted for comparison. The SC is composed of 40% quartz and
783 60% feldspar, with $\delta^{30}\text{Si} = -0.25\text{‰}$ and Al/Si = 0.25. Scenarios A, B and C show various phase
784 transformations in the starting material: A) loss of feldspar/accumulation of quartz; B) replacement of
785 feldspar by smectite ($\delta^{30}\text{Si} = -1.1\text{‰}$; Al/Si = 0.67) and loss of 25% of detrital quartz; C) replacement
786 of feldspar by kaolinite ($\delta^{30}\text{Si} = -2.0\text{‰}$; Al/Si = 1.0) and loss of 60% of detrital quartz. Much of the
787 shale data lie on or close to lines B and C, suggesting secondary mineral formation and abundance of
788 detrital quartz are major controls over shale Si isotope composition. Scenario D shows simple mixing
789 between the SC and a biogenic silica source ($\delta^{30}\text{Si} = +1.24\text{‰}$; Al/Si = 0) and implies that only ~10%
790 incorporation of such material is needed to explain the heavier isotopic compositions of some of the
791 shales. See text for discussion.

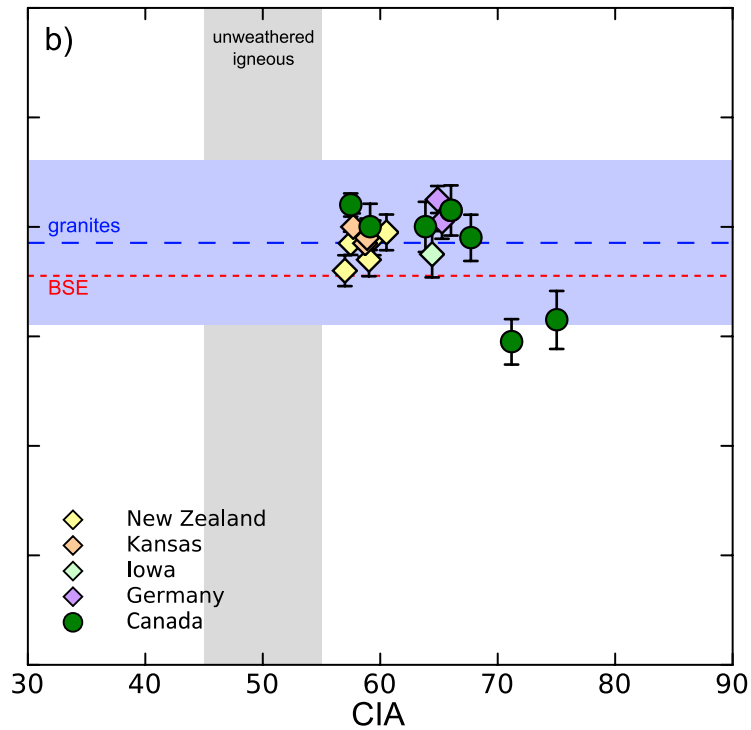
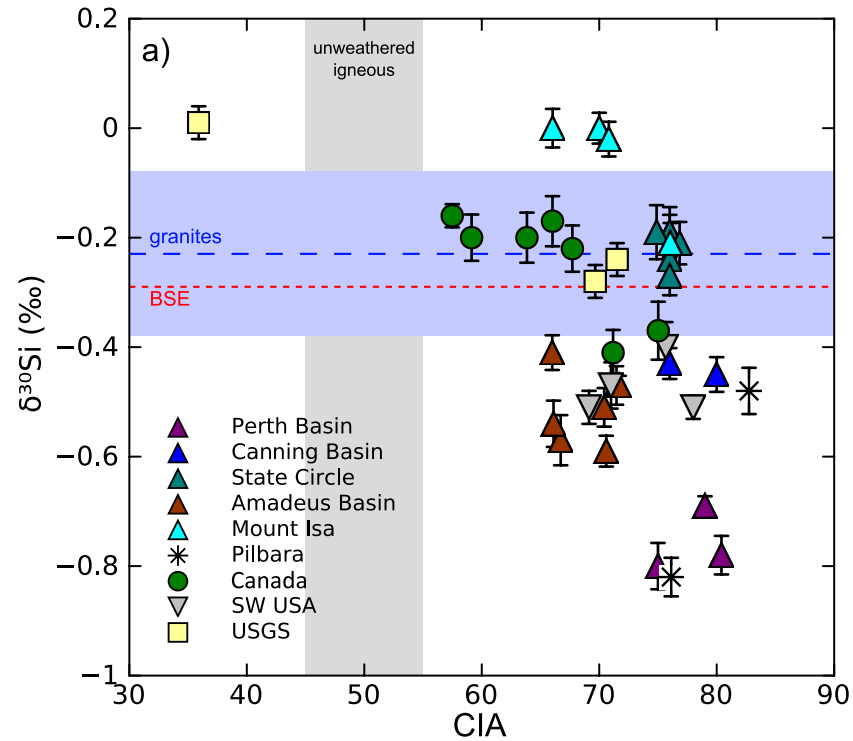
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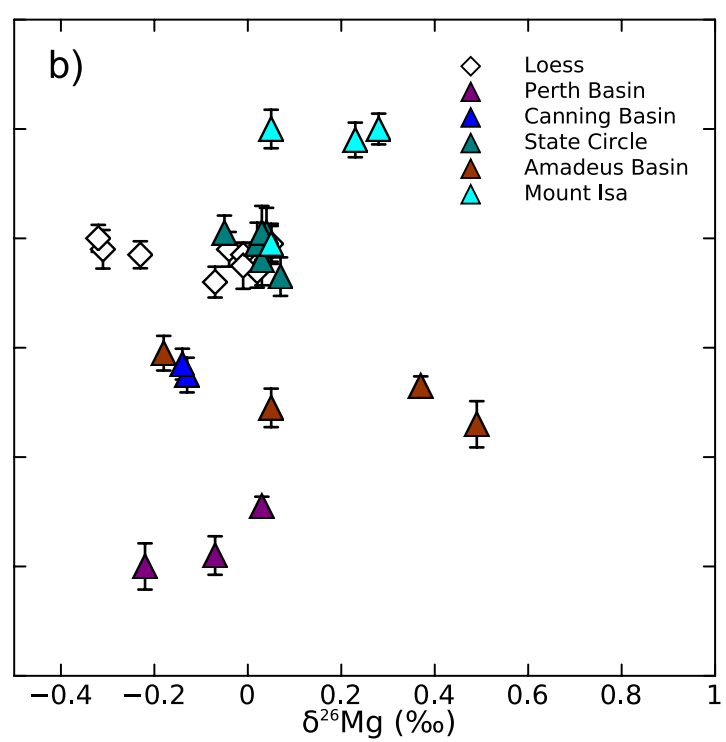
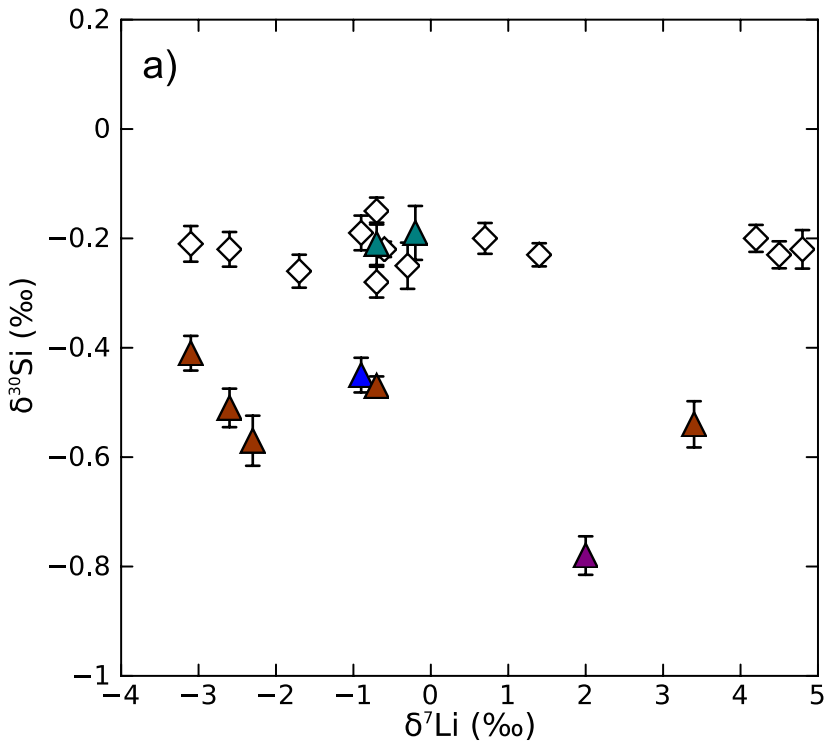
793 **Figure 7:** Histogram of the $\delta^{30}\text{Si}$ values of the upper crustal lithologies analysed in this study and the
794 granite study of Savage et al. (2012). One clear peak, around $\delta^{30}\text{Si} = -0.25$ to -0.20‰ , is defined
795 mainly by the granites and loess samples. This peak also coincides with the weighted average $\delta^{30}\text{Si}$

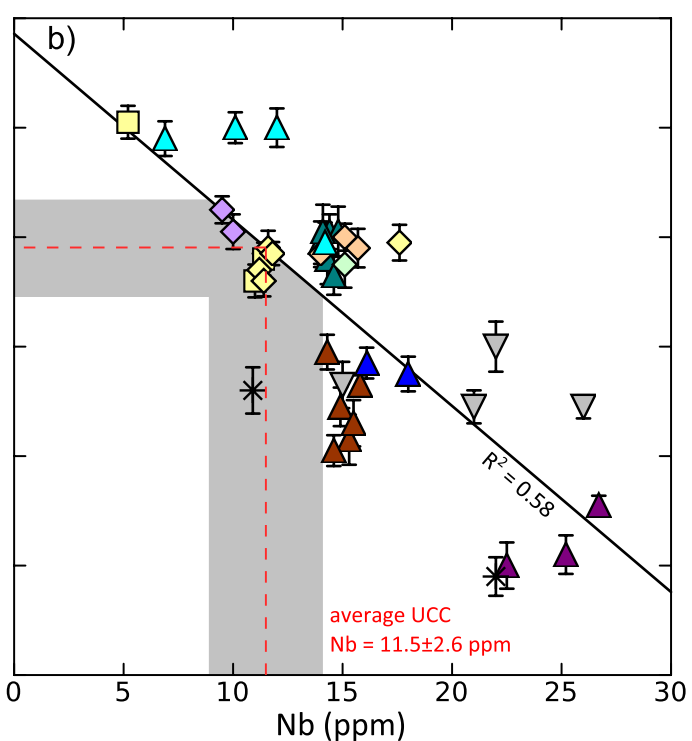
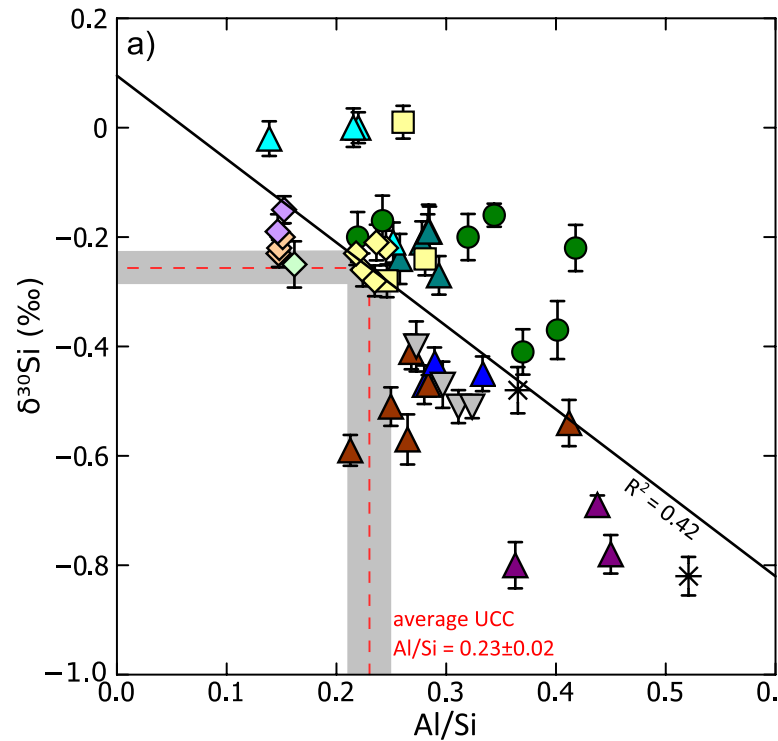
796 value for the upper continental crust. BSE average is taken from Savage et al. (2010).

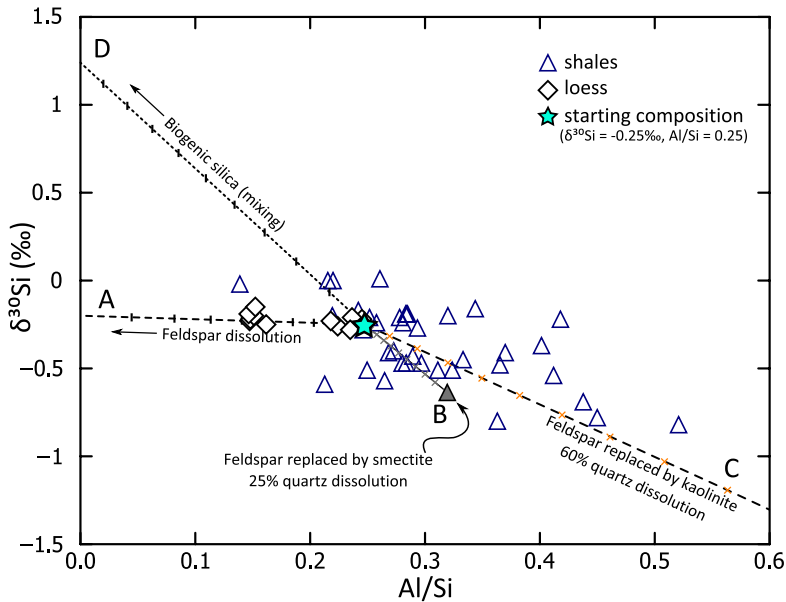












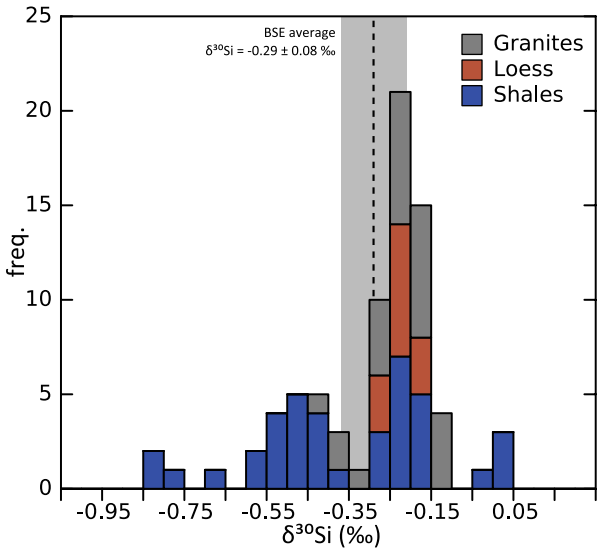


Table 1.

Silicon isotope data for external standards analysed during this study, as well as literature values for said standards. Numbers refer to repeat analysis of the same solution. Errors are given as both 2 s.d. ($2 \times$ standard deviation) and 95% s.e. (95% standard error of the mean = $t \times \text{s.d.}/(n)^{1/2}$, where t = inverse survival function of the Student's t-test at the 95% significance level, and $n-1$ degrees of freedom).

Standard		SiO ₂ (wt.%)	δ ³⁰ Si (‰)	2s.d.	95%s.e.	δ ²⁹ Si (‰)	2s.d.	95%s.e.	<i>n</i>
Diatomite	1	100	1.22	0.11	0.04	0.64	0.07	0.02	11
	2		1.23	0.09	0.03	0.62	0.06	0.02	11
	3		1.22	0.07	0.02	0.64	0.07	0.02	11
	4		1.21	0.04	0.02	0.59	0.05	0.02	11
	5		1.20	0.08	0.03	0.61	0.07	0.02	11
	6		1.25	0.08	0.03	0.63	0.07	0.02	11
	7		1.23	0.10	0.04	0.63	0.07	0.02	11
	8		1.20	0.06	0.02	0.63	0.03	0.01	11
	9		1.22	0.09	0.03	0.62	0.08	0.03	11
	10		1.24	0.11	0.04	0.61	0.07	0.02	10
	11		1.23	0.10	0.03	0.65	0.11	0.04	11
	12		1.20	0.10	0.04	0.61	0.05	0.02	9
Mean and external reproducibility			1.22	0.03		0.62	0.03		12
Reynolds et al. (2007)			1.26	0.20		0.64	0.14		
Georg et al. (2009a)			1.23	0.16		0.62	0.11		
Savage et al. (2011)			1.23	0.10		0.64	0.08		
SGR-1b	1	28.2	0.01	0.04	0.01	-0.01	0.06	0.02	11
Hughes et al. (2011)			0.03	0.09		0.02	0.03		
BHVO-2	1	49.9	-0.31	0.05	0.02	-0.14	0.08	0.03	11
	2		-0.34	0.10	0.03	-0.15	0.06	0.02	11
	3		-0.29	0.06	0.02	-0.18	0.04	0.01	11
	4		-0.26	0.05	0.02	-0.13	0.07	0.02	11
	5		-0.29	0.07	0.02	-0.17	0.06	0.02	11
	6		-0.31	0.08	0.03	-0.14	0.03	0.01	11
	7		-0.31	0.10	0.03	-0.15	0.09	0.03	11
	8		-0.29	0.12	0.04	-0.16	0.07	0.02	11
	9		-0.31	0.08	0.03	-0.17	0.08	0.03	10
	10		-0.33	0.10	0.04	-0.16	0.09	0.03	9
	11		-0.28	0.06	0.02	-0.15	0.04	0.01	11

	12	−0.30	0.10	0.03	−0.17	0.06	0.02	11
Mean and external reproducibility	−0.30	0.04			−0.16	0.03		12
Abraham et al. (2008)	−0.29	0.11			−0.17	0.04		
Zambardi and Poitrasson (2011)	−0.27	0.08			−0.14	0.05		
Savage et al. (2011)	−0.29	0.09			−0.15	0.08		

Table 2.

Silicon isotope data for loess samples analysed in this study. Major element data and CIA values are taken from Taylor et al. (1983). Magnesium and lithium stable isotope data are taken from Li et al. (2010) and Teng et al. (2004) respectively.

Sample	ID	SiO ₂ (wt. %)	δ ³⁰ Si (‰)	2s.d.	95%s.e.	δ ²⁹ Si (‰)	2s.d.	95%s.e.	n	CIA	δ ²⁶ Mg (‰)	δ ⁷ Li (‰)	Al/Si
<i>Banks Peninsula, New Zealand</i>	BP-1	72.7	-0.22	0.09	0.03	-0.12	0.06	0.02	11	59	-0.04	-2.6	0.25
	BP-2	74.0	-0.26	0.08	0.03	-0.12	0.04	0.02	10	59	0.02	-1.7	0.22
	BP-3	72.5	-0.21	0.08	0.03	-0.08	0.06	0.02	9	61	0.05	-3.1	0.24
	BP-4	74.0	-0.23	0.06	0.02	-0.12	0.07	0.02	11	57	-0.01	1.4	0.22
	BP-5	72.5	-0.28	0.08	0.03	-0.11	0.05	0.02	11	57	-0.07	-0.7	0.23
<i>Kansas, USA</i>	CY-4a-A	80.4	-0.23	0.07	0.02	-0.12	0.11	0.04	11	59	-0.23	4.5	0.15
	CY-4a-B	80.8	-0.22	0.10	0.04	-0.12	0.07	0.02	11	59	-0.31	4.8	0.15
	CY-4a-C	79.9	-0.20	0.07	0.02	-0.10	0.04	0.01	11	58	-0.32	4.2	0.15
<i>Muscatine, Iowa, USA</i>	I	79.5	-0.25	0.12	0.04	-0.13	0.02	0.02	11	64	-0.01	-0.3	0.16
<i>Kaiserstuhl, Germany</i>	K1	59.9	-0.19	0.09	0.03	-0.09	0.06	0.02	11	65		-0.9	0.15
	K2	59.1	-0.15	0.07	0.02	-0.08	0.06	0.02	11	65		-0.7	0.15
<i>Hungary</i>	H	52.0	-0.22	0.04	0.01	-0.14	0.04	0.01	11			-0.6	
<i>China</i>	CH	56.0	-0.19	0.11	0.04	-0.11	0.07	0.03	10			0.7	
	CH-repeat		-0.20	0.08	0.03	-0.08	0.08	0.03	11				

Table 3.

Silicon isotope data for shale samples analysed in this study. Silica contents (in wt. %) and deposition ages are taken from Taylor and McLennan (1976), McLennan et al., (1995) and the USGS datasheets (<http://minerals.cr.usgs.gov/>). CIA values are taken directly from, or calculated using the chemical analyses provided in the above papers. Magnesium and lithium stable isotope data are taken from Li et al. (2010) and Teng et al. (2004) respectively.

Sample	ID	SiO ₂ (wt.%)	$\delta^{30}\text{Si}$ (‰)	2s.d.	95% s.e.	$\delta^{29}\text{Si}$ (‰)	2s.d.	95% s.e.	<i>n</i>	CIA	$\delta^{26}\text{Mg}$ (‰)	$\delta^7\text{Li}$ (‰)	Al/Si
<i>Post-Archaean Australian shales</i>													
<i>Perth Basin</i> (200-250 Ma)	PW-4	57.9	-0.69	0.05	0.02	-0.37	0.11	0.04	11	79	0.02		0.44
	PW-5	55.3	-0.78	0.10	0.04	-0.41	0.08	0.03	11	80	-0.07	2.0	0.45
	PW-7	59.6	-0.80	0.12	0.04	-0.41	0.13	0.05	11	75	-0.22		0.36
<i>Canning Basin</i> (250-400 Ma)	PL-1	63.5	-0.45	0.09	0.03	-0.21	0.07	0.02	11	80	-0.13	-0.9	0.33
	PL-6	61.1	-0.43	0.08	0.03	-0.25	0.03	0.01	11	76	-0.14		0.29
	PL-7	66.8	-0.47	0.10	0.04	-0.22	0.05	0.02	11	71			0.28
<i>State Circle</i> (440 Ma)	SC-1	65.1	-0.19	0.09	0.03	-0.09	0.08	0.03	11	76	-0.05		0.28
	SC-2	65.3	-0.19	0.13	0.05	-0.08	0.10	0.04	11	76	0.04		0.28
	SC-3	67.0	-0.24	0.13	0.05	-0.15	0.07	0.02	11	76	0.03		0.26
	SC-5	65.3	-0.27	0.10	0.04	-0.14	0.12	0.04	11	76	0.07		0.29
	SC-7	65.6	-0.21	0.11	0.04	-0.14	0.04	0.01	11	77	0.02	-0.7	0.28
	SC-8	65.6	-0.19	0.14	0.05	-0.11	0.08	0.03	11	75	0.03	-0.2	0.28
<i>Amadeus Basin</i> (850 Ma)	AO-6	61.1	-0.41	0.09	0.03	-0.22	0.07	0.02	11	66	-0.18	-3.1	0.27
	AO-7	61.8	-0.57	0.13	0.05	-0.28	0.10	0.04	11	67		-2.3	0.26

	AO-8	70.0	-0.59	0.08	0.03	-0.31	0.08	0.03	11	71			0.21
	AO-9	65.8	-0.51	0.10	0.04	-0.29	0.08	0.03	11	70	0.05	-2.6	0.25
	AO-10	63.0	-0.47	0.05	0.02	-0.27	0.03	0.01	11	72	0.37	-0.7	0.28
	AO-12	56.6	-0.54	0.12	0.04	-0.28	0.05	0.02	11	66	0.49	3.4	0.41
<i>Mt. Isa</i> (1500 Ma)	MI-1	71.0	0.00	0.08	0.03	-0.01	0.07	0.02	11	70	0.28		0.22
	MI-2	56.1	-0.02	0.09	0.03	-0.01	0.06	0.02	11	71	0.23		0.14
	MI-4	69.8	0.00	0.10	0.04	-0.02	0.07	0.02	11	66	0.05		0.22
	MI-5	65.9	-0.21	0.09	0.04	-0.14	0.09	0.04	9	76	0.05		0.25
<i>Pilbara Archaean shales - Australia</i>													
	Gorge Creek (3.4 Ga) Pg-7	57.6	-0.82	0.10	0.04	-0.41	0.08	0.03	11	76			0.52
	Whim Creek (2.7 Ga) WC-3	48.1	-0.48	0.12	0.04	-0.21	0.09	0.03	11	82			0.37
<i>Huronian – Canada (2.5 – 2.2 Ga)</i>													
McKim	M-5	58.5	-0.37	0.13	0.05	-0.21	0.05	0.02	9	75			0.40
Pecors	P-7	56.6	-0.22	0.12	0.04	-0.09	0.11	0.04	11	68			0.42
Gowganga	G-9	59.9	-0.20	0.12	0.04	-0.09	0.04	0.01	11	59			0.32
	<i>G-9repeat</i>		-0.18	0.09	0.03	-0.07	0.04	0.02	10				
	G-16	57.7	-0.16	0.06	0.02	-0.07	0.05	0.02	11	57			0.34
	G-28	57.6	-0.41	0.11	0.04	-0.21	0.11	0.04	10	71			0.37
Gordon Lake	GL-3		-0.17	0.13	0.05	-0.10	0.07	0.02	11	66			0.24
<i>Sudbury Basin – Canada (1.85 Ga)</i>													
Chelmsford	DKM-6	68.9	-0.20	0.13	0.05	-0.10	0.06	0.02	11	64			0.22
<i>SW USA Proterozoic (1.8 -1.7 Ga)</i>													
Rinconada	R1-1	65.6	-0.51	0.08	0.03	-0.30	0.05	0.02	10	69			0.31
	R4-5	64.8	-0.51	0.06	0.02	-0.27	0.10	0.04	11	78			0.32

Piedra Lumbra	PL-5	68.0	-0.47	0.12	0.04	-0.26	0.13	0.05	11	71	0.30
Uncomphagre	S-4	67.4	-0.40	0.13	0.05	-0.22	0.08	0.03	11	76	0.27
<i>USGS shale standards</i>											
Ohio - Devonian	SDO-1	49.3	-0.24	0.04	0.01	-0.10	0.07	0.02	11	72	0.28
Cody - Cretaceous	SCo-1	62.8	-0.28	0.03	0.01	-0.17	0.04	0.01	11	70	0.25
Gren River - Eocene	SGR-1b	28.2	0.01	0.04	0.01	-0.01	0.06	0.02	11	36	0.26

Table 4.

Estimate of the weighted average Si isotopic composition of the upper continental crust, as well as calculated $\delta^{30}\text{Si}$ averages for the component lithologies. Lithological units, proportions and SiO_2 contents are taken from Wedepohl (1995), except for the sedimentary sub-unit SiO_2 contents, which were estimated using the samples analysed in this study. The sedimentary $\delta^{30}\text{Si}$ was calculated using data from this research; the felsic intrusive unit was constrained using data from Savage et al. (2012); the $\delta^{30}\text{Si}$ value of the gabbroic unit is the BSE value (Savage et al., 2010).

Rock Unit	Proportion in upper crust (%)	Avg. SiO_2 (wt.%)	$\delta^{30}\text{Si}$ (‰)	2s.d.
Sedimentary	14	52.4	-0.31	0.26
Sub-units of which				
Shales, siltstones	6	61.7	-0.36	0.44
Sandstones	3	73.2	-0.22	0.07
Mafic volcanics	3	50.1	-0.29	0.08
Carbonates	2	0	-	-
Felsic intrusive	50	69.2	-0.23	0.15
Gabbro	6	50.1	-0.29	0.08
Metamorphic	30	63.7	-0.25	0.16
Upper continental crust		64.1	-0.25	0.16